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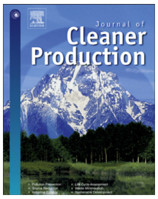

Slow pyrolysis of relevant biomasses in the Mediterranean basin. Part 1. Effect of temperature on process performance on a pilot scale

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ABSTRACT

The present study focused on assessing the effect of the temperature (350, 450 and 550 °C) on the pyrolysis performance of several biomasses: olive stone, almond shell, pine wood and olive-tree pruning. First, they were subjected to thermogravimetric and Differential Scanning Calorimetric analyses to determine their thermal decomposition and heat flux. Afterwards, several tests were performed in a pilot plant reactor for char production. Moreover, a characterisation of the pyrolysis products and an assessment of both energy requirements and potentially energy self-sufficient process were performed. Our results show that the process was feasible with low grade pretreated biomass and it would become self-sufficient with the energy from gas and liquid fractions at 350 °C. The analyses of the char samples (proximate, elemental and organic carbon (C_{org}) analyses) show that almost all of them had features indicating that they were “biochar”, suggesting high stability at higher formation temperatures based on their molar ratios (H/C_{org}; O/C_{org}). However, a more detailed characterisation is necessary to assess the quality of char as a soil amendment.

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1. Introduction

In recent years, there has been increasing concern over biomass processing via pyrolysis because a new product has become relevant due to its attractive advantages. This product is named “biochar” and is defined as “a charcoal-like substance that is pyrolysed from sustainable obtained biomass under controlled conditions and which is used for any purpose which does not involve its rapid mineralisation to CO_2” (EBC, 2013). Currently, the research regarding biochar production conditions is a challenging area that requires the development of a technology capable of generating a product with the following requirements for environmental management (Lehmann and Joseph, 2009):

- Waste management. The role of agriculture in mitigating climate change provides new opportunities for adding value to organic waste through management processes, such as pyrolysis, integrating these processes into a sustainable agriculture-bioenergy production system (Laird et al., 2010). Pyrolysis can act as a waste management system that uses residual biomass as a feedstock that is currently improperly managed or unsuitable for conventional applications.
- Climate change mitigation. A nearly net zero carbon cycle is offered when biomasses are fed into pyrolysis processes. If biochar is added to soil, the carbon cycle might have a positive impact on the environment, reducing the CO_2 emission in the atmosphere and thus becoming a carbon sink. Furthermore, adding biochar to soil can reduce N_2O and CH_4 emissions from cultivated soils (Barrow, 2012; Karhu et al., 2011).
- Energy production from renewable energy sources. Apart from the solid fraction, pyrolysis also generates gas and liquid fractions (Neves et al., 2011) that might be a source of energy. The gas fraction from pyrolysis and gasification processes contains several combustible gases that might have energetic applications (Nguyen et al., 2013) including downstream gas turbine/gas engine, combustion for power generation or substitution for natural gas after proper treatment (Chen et al., 2003), supplying a portion of the energy required for the pyrolysis plant (Gañan et al., 2006). Moreover, the liquid fraction might be used to generate power (Ning et al., 2013) depending on its initial properties (Chiaramonti et al., 2007). These fractions might also be used as a feedstock for the chemical industry. Nevertheless,

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the commercialisation of special chemicals from bio-oils requires reliable low cost separation and refining techniques (Zhang et al., 2007).

- Soil improvement. Using biochar as a soil amendment might be a viable option for sustainable agriculture because it might be a long-term sink for carbon in soil with benefits for crops, enhancing the efficiency of nutrient and water use (Barrow, 2012). Various residual biomasses can be used as a feedstock for biochar production. In the present study, olive-tree pruning, olive stone, almond shell and pine wood were evaluated because Spain is one of the major olive and almond producers worldwide, generating approximately seven million tons of olives and two hundred thousand tons of almonds in 2011 (FAOSTAT, 2012); also extensive timber areas generate large quantities of wood residue (around twenty five millions of cubic meters; FAOSTAT, 2012). Consequently, copious quantities of waste are available from harvesting or production processes. These biomasses have previously undergone pyrolysis treatment; however, most studies were performed on a laboratory scale toward other purposes (Zabaniotou et al., 2008; Caballero et al., 1997; Kang et al., 2006).

The primary objective of this work was to assess the effect of the feedstock source and the temperature on the performance of pyrolysis process, by considering both the mass and energy balances to define the biochar production process in a pilot plant. The energy applicability has been estimated for the gas and liquid fractions.

2. Materials and methods

The following residual biomasses were tested because they are widely available in the Mediterranean area and are produced in large quantities: olive stone (OSB), almond shell (ASB), pine wood (as pellets, PWB) and olive-tree pruning (OPB). OSB, OPB and ASB were provided by “BIOTERM AGROFORESTAL SL” (Córdoba, Spain), while PWB was provided by “AMATEX SA” (Soria, Spain).

2.1. Materials

The chemical composition was expected to vary because OPB and PWB are categorised as woody biomass, while OSB and ASB are categorised as agricultural biomass according to their biological diversity, source and origin (Vassilev et al., 2012).

The sampling method to ensure representative samples of the different types of biomass was performed following UNE-CEN/TS 14780.

For the thermobalance tests, the four raw materials were ground and shaken for 3 min in a laboratory ball mill and subsequently passed through a 0.25 mm mesh. For the pilot plant reactor tests, the raw feedstock samples were air-dried (moisture $< 10\%$) and treated as received: between 32 and 40 mm long, and 1–3 mm thick for ASB; between 3 and 7 mm long, and 3–5 mm thick for OSB; between 30 and 70 mm long, and 2–20 mm thick for OPB; between 15 and 45 mm long and 0.6 mm in diameter for PWB from waste sawmill material.

2.2. Methods

The methodology to study the effect of temperature on pyrolysis process performance of several biomasses includes test from thermogravimetric equipment as small scale tests to understand the behaviour of the material, to pyrolysis tests in a pilot plant to study them in large scale; as well as the main characterisation of the obtained products to know their features.

2.2.1. Thermobalance equipment

The thermogravimetric analyses were performed with a TA Instruments thermobalance (model SDT Q600, TA Instruments-Waters LLC, New Castle, Delaware, USA). Samples (5.75 ± 0.25 mg) were pyrolysed at 15 °C/min up 750 °C after being placed in alumina crucibles under an inert atmosphere and 100 mL/min flowing nitrogen. The temperature, weight loss and heat flux were processed with Universal analysis 2000 (V4.5A software from TA Instruments-Waters LLC, New Castle, Delaware, U.S.A.) to generate the thermogravimetric (TGA) and Differential Scanning Calorimetric (DSC) curves. The experiments were replicated at least twice, and the error of the experimental results was ±3%.

2.2.2. Pilot plant reactor

Kiln reactors seem to have advantages for solid treatments (Kern et al., 2012), making them appropriate for biochar production in large scale. Although most of the lab scale experiments usually work from room temperature to a settled temperature (Agrafioti et al., 2013; Lee et al., 2013; Sun et al., 2014) that fact limits the production.

Thus, the pilot plant experiments were carried out in a semi-continuous, electrically heated reactor fed through a hopper with a system of two valves designed to ensure oxygen-free conditions for each partial load. A scheme describing the reactor is shown in Fig. 1.

The reactor consisted of a single cylindrical chamber (1.415 m long × 0.290 m inner diameter) with three independently heated zones. The reactor utilised several thermocouples to measure the working temperature. This feature allowed for automatic adjustments to the temperature and heat distribution along the reactor. The material moves through the reactor using an endless screw 0.280 m in diameter.

The pyrolysis gases were driven to flare using an extractor fan that produced a slight vacuum inside the reactor.

The sampling set-up included a bubbler and two “U” shaped glass tubes filled with Raschig rings in an ice bath to cool the gas and separate the condensable fraction. A vacuum pump was used to overcome the gas flow inside the tubes generated by the extractor fan. The produced gases were sampled and analysed offline using gas chromatography.

The solid fraction was collected in a container at the bottom of the reactor, and weighed after cooling. The condensates were collected downstream from the extractor fan and weighed. The percentage of the gas fraction was calculated using the difference. The experiments were replicated at least twice. The tests were performed with 10 kg samples.

The conventional pyrolysis has a wide range of working conditions using moderate temperatures (up to 600 °C) to produce biochar (Basu, 2010). Thus, the working temperatures were set at 350, 450 and 550 °C.

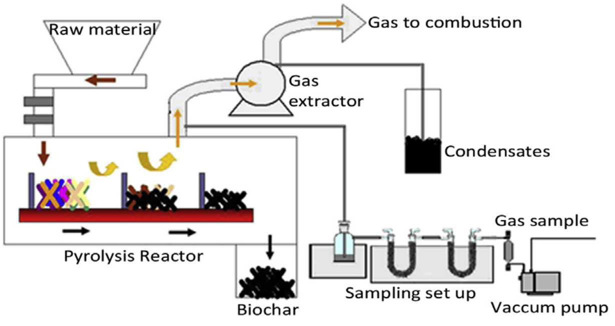

Fig. 1. Pilot plant reactor scheme.

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The residence time of the raw material is a parameter that depends on the pyrolysis techniques, but a comprehensive review of modern slow pyrolysis techniques is still missing (Harsono et al., 2013) to compare those working conditions. Thus, residence time of 15 min has been established based on experience (Sánchez et al., 2007a,b), and getting a carbon content in the solid fraction higher than 50%, recommended by EBC guidelines (EBC, 2013) for biochar production. An equilibrium between energy consumption (linked with the residence time) and energy output is also taken into account for this residence time and the assessment of a self-sustainable process.

The energy required to heat the reactor to the working temperature was assumed to be constant: 10.54, 16.27 and 23.51 kWh to reach 350, 450 and 550 °C, respectively. The energy consumed during each test was registered; it was the sum of the energy required for the pyrolysis plus the heat loss of the reactor.

2.2.3. Analysis techniques

Three main products are obtained from the pyrolysis process, gas, solid and liquid fractions that should be properly characterised to understand the effect of the temperature under the pyrolysis process of several biomasses. Thus, each product has been analysed to know the influence of the temperature and the type of raw material in the final products.

2.2.3.1. Gas fraction. The gas samples were analysed in an HP 5890 chromatograph (HP-Agilent, Santa Clara, California, U.S.A.) using three separation columns and two detectors. An HP-AL/S semi-capillary column was used (50 m long × 0.35 mm inner diameter) to analyse the hydrocarbons (C_xH_y) while using helium as the carrier gas and a flame ionisation detector (FID). A 5 Å molecular exclusion column was employed (1.83 m long × 3.175 mm outer diameter) with a mesh size of 60/80 to separate H_2, O_2, N_2, CH_4 and CO. Helium was the carrier gas and a thermal conductivity detector (TCD) was included. The CO_2 concentration was determined with a Chromosorb 102 packed column (1.83 m long × 3.175 mm outer diameter) with a mesh size of 80/100 while using He as the carrier gas; a TCD was used for this measurement. Once the composition of the gases was quantified, the heating values and densities were estimated according to UNE-EN ISO 6976.

2.2.3.2. Solid fraction. The raw materials and solid fractions obtained after pyrolysis were characterised. A proximate analysis was performed according to ASTM 3302, UNE 3219 and UNE 32004 for the total moisture, volatile matter and ashes, respectively. The ultimate composition analysis was also performed to account for the major chemical elements presented in the sample: C, H, N, S and O. A LECO CHN-600 analyser (all LECO equipment is from LECO Corporation, St. Joseph, Michigan, USA) was used to determine the first three elements, according to ASTM 5373. The inorganic carbon was determined according to TMECC (2002). The organic carbon (C_{org}) was obtained subtracting the inorganic carbon from total carbon (C). The total S content was determined with a LECO SC-132 analyser according to ASTM 4239. The O content was obtained by subtraction. The heating value was obtained with a LECO AC-300 analyser using an adiabatic method according to UNE 32006.

2.2.3.3. Liquid fraction. Two phases (heavy and light) were identified in the liquid fraction; these phases exhibited different density and viscosity properties visually and were successfully separated using decantation. The light phase was only considered for the mass balance due to its high water content. The water content of both heavy and light phases was determined using the dragging toluene technique, according to UNE 51027. The heating value was determined using ASTM 240-09.

3. Results and discussion

The behaviour of the biomass under pyrolysis depends on several factors such as: the origin of the biomass, the way it is presented, the selected equipment, and the pyrolysis conditions (mainly residence time and temperature). This fact affects the different product yields and features that are going to be study along the next sub sections.

3.1. Biomass characterisation

The characterisation of the biomass provides some background knowledge regarding the behaviour of the biomass and how that behaviour may affect the products obtained from the pyrolysis process. The characterisation of the four materials is shown in Table 1. The volatile matter content ranged from 78 to 84 %. The typical biomass values range from 65 to 85 % (Yang et al., 2005); these values are much higher than those of coal. Therefore, these materials are easy to ignite, even at relatively low temperatures (Neves et al., 2011). The fixed carbon also correlates with the common biomass values reported by other authors (Neves et al., 2011); these values range from 15 to 20 % as can be seen in Table 1. The elemental composition ranged from 49 to 51 % carbon, 42–44 % oxygen and approximately 6% hydrogen, similar to previous studies reporting intervals from 40 to 60 % carbon, from 30 to 50 % oxygen and from 5 to 8 % hydrogen (Neves et al., 2011). The nitrogen and sulphur contents are low in most samples. Consequently, these materials produce few NO_x and SO_2 emissions during oxidation.

The molar H/C and O/C ratios were related to energy availability and were approximately 1.4 and 0.7, respectively. These values are similar earlier studies (Jenkins et al., 1998). The high molar H/C and O/C ratios imply that the energy from the biomass is limited due to the lower energy contained in the C–O and C–H bonds relative to the C–C bonds (Gañán et al., 2006a,b). The coalification diagram representing the molar H/C and O/C ratios from biomass to anthracite coal indicated that fossil fuels have lower molar H/C (0.20–1.00) and O/C ratios (0.02–0.25) (Baxter, 1993). Therefore, the low heating values (LHV) are higher than those of the biomass. The ASB, OSB, OPB and PWB comprise heating values between 17 and 21 MJ/kg (as shown Table 1).

3.2. Thermogravimetric and Differential Scanning Calorimetric tests

The DSC curves exhibit the heat flux (W/g) that biomasses require or transfer versus temperature and time. According to Rath

Table 1
Characterisation of almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses.

Feedstock	ASB	OSB	OPB	PWB
Moisture	7.63	7.91	8.09	6.77
Volatile matter[a]	82.14	78.36	79.67	83.83
Ash[a]	0.55	1.40	3.73	0.56
Fixed carbon[a,c]	17.31	20.24	16.60	15.61
C[b]	49.27	49.79	50.91	50.18
H[b]	6.06	6.07	6.03	6.08
N[b]	0.12	0.10	0.60	0.20
S[b]	0.05	0.06	0.07	0.05
O[b,c]	44.49	43.98	42.39	43.48
H/C ratio	1.47	1.45	1.40	1.44
O/C ratio	0.68	0.66	0.65	0.65
LHV (MJ/kg)	17.92	17.94	17.55	20.96

[a] Percentage on a dry basis.
[b] Percentage on a dry, ash-free basis.
[c] Calculated by difference.

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et al. (2003), the heat of pyrolysis ranges from endothermic to large exothermic values. The typical biomass flux energies during pyrolysis are characterised by the following steps: drying, heating, biomass degradation and finally heating and aggregating the char (He et al., 2006). The DSC flux of pyrolysis has been study without differ between "heat of reaction" and "specific heat" of the solid in order to study the global behaviour of the system and compare the behaviour of several biomasses under the same conditions. Thus, a "zero" measured heat flux is a region where the specific heating of the material is balanced by exothermic heat. The terms that define those regions have been defined as "apparent" exothermic/endothermic heats.

Fig. 2 illustrates the results of the DSC tests performed with OSB, ASB, PWB and OPB where these steps can be identified. The drying step ranged from ambient temperatures to 105 °C. The biomasses showed close heat flux ranges, due to their similar water contents (6–9 %, Table 1). To determine the calorific requirements (kJ/kg), the integration limits were adjusted from 120 to 650 °C to relieve any possible uncertainty in the data. The lowest limit (120 °C) was set to remove the effect of the moisture on the heat flux during the integration. In addition, the upper limit (650 °C) was selected to be above the highest operating temperature. The heating step began at 105 °C and ended at different temperatures between 250 and 300 °C. The poorly defined limits between the end of this stage and the beginning of the biomass degradation were detected. The OSB and ASB were the first to begin the degradation step. The OSB oscillated between slightly apparent exothermic to endothermic values. This early apparent exothermic heat flux affected the total calorific requirements, which seemed to be the lowest. This behaviour was different from the rest of biomasses, which only showed a large apparent endothermic phase. The heating and aggregation of char (final step) showed a transition from apparent endothermic to exothermic behaviour due to the competition between endothermic reactions such as devolatilisation and the exothermic primary char formation (Rath et al., 2003). Table 2 shows the energy required at 350, 450 and 550 °C from the thermogravimetric tests. The energy requirements (kJ/kg) increased with the temperature, following a trend almost doubling from 350 to 450 °C and between tripling or quadrupling from 350 to 550 °C. Furthermore, the energy consumption was higher for woody (PWB and OPB) than agricultural biomasses (ASB and OSB).

The TG and DTG curves (Fig. 3) provide the decomposition profiles of the treated biomasses, which are well-known for lignocellulosic materials (Pasangulapati et al., 2012; Yang et al., 2007). Although similar behaviours were expected, some differences were identified. The OSB lost most of its volatile matter at lower temperatures relative to OPB, ASB and WPB; these materials also exhibited the lowest release of volatiles. Conversely, the PWB required the highest temperatures and underwent further devolatilisation. Consequently, the residual mass was: 21.10, 18.70, 16.83 and 13.88% for OSB, OPB, ASB and WPB, respectively.

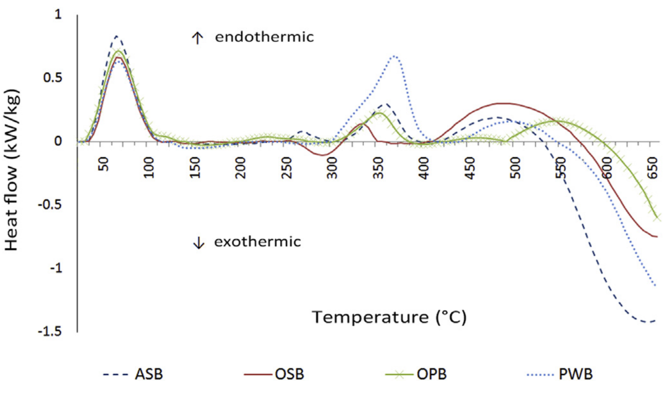

Fig. 2. DSC curves for almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses.

Both phenomena (energy consumption and mass loss) were linked with the lignocellulosic composition of biomass. The general composition of biomasses ranges between 40 and 50% cellulose, 20-40 hemicellulose and 10–40% hemicellulose (McKendry, 2002).

The cellulose, hemicellulose and lignin have specific DTG profiles. The cellulose decomposes over a narrow temperature range (280–360 °C) showing its faster decomposition peak at 339 °C. The hemicellulose decomposes with two distinct peaks one a t 246 and one at 295C between 200 and 320 °C. Finally, the lignin decomposes over a very large range (140–600 °C) with a low intensity peak at 380 °C (Carrier et al., 2011). According to these peaks, these compounds can be identified on DTG curves of crude biomasses and their relative intensities can be related to the global quantities of hemicellulose, cellulose and lignin (Carrier et al., 2011).

The characteristic shoulder of hemicellulose (at ~246 °C and ~295 °C) was identified with higher intensity of mass loss in case of OSB and ASB than in PWB and OPB. These meant a higher relative hemicellulose content. This fact could be related with the lower consumption energy. The hemicellulose structure and bounds are less complex than cellulose and lignin (Mohan et al., 2006), requiring less energy consumption and less temperature to break them.

The OPB and PWB also showed different profiles between their DTG curves. The OPB seemed to have a combined profile between its major components whilst PWB seemed to have a greater and fitted shape with cellulose profile and poor influence of hemicellulose and lignin. It could be associated with its high consumption energy and its lower carbonised residue. Stefanidis et al. (2014) showed the behaviour of cellulose, hemicellulose and lignin under pyrolysis and found the lower yield content of char for the cellulose and the higher for lignin. Thus, PWB seemed to have high cellulose content pointed by its DTG profile and low char content. The complexity combination of the major components didn't allow identifying the residue trend with the rest of biomasses.

3.3. *Pilot plant test*

The pilot plant studies include the assessment of product yield, and energy balances, as well as the definition of the properties of the pyrolysis products remarking the features of the solid fraction.

3.3.1. *Product yields*

The yield of the fractions produced during the pyrolysis process changed depending on several parameters, such as residence time, particle size and temperature. The residence time was pre-set as 15 min for all of the tests based on experience (Sánchez et al., 2007a,b) to remove any variability associated with the residence time.

The particle size varied among materials because it was intended to treat them as received. According to Asadullah et al. (2010) during pyrolysis, the tar concentration in the pyrolysing biomass/char matrix increases with increasing particle size and the high tar concentration implies intensive recombination of tarry compounds on the internal surface of the pyrolysing biomass/char particle, resulting in reduced weight loss. Thus, particle size may be a relevant factor in pyrolysis performance and product yield affecting the matter and heat transmission phenomena.

Regarding the temperature, trend for the yields was determined for most of the cases. Table 3 reports the yields for the three working temperatures in the pilot plant reactor. The char gradually decreased at higher working temperatures, similar to the liquid

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Table 2
Energy requirements for almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses at the three studied temperatures, during thermogravimetric analysis and pilot plant treatment.

Feedstock T (°C)	ASB			OSB			OPB			PWB		
	350	450	550	350	450	550	350	450	550	350	450	550
Thermogravimetry												
Required Energy (kJ/kg)	357	718	1142	255	499	880	357	764	1276	581	1160	1741
Pilot plant												
Electrical Required Energy (kJ/kg)	814	1753	2657	1793	1782	1300	1588	2473	2974	1800	1732	1944
Feeding rate (kg/h)	10	10	10	10	10	10	5	5	5	8	8	8

fraction, while the gas yield increased. These behaviours may be attributed to the increase in the devolatilisation of the organic material and the secondary cracking reactions of the condensable vapours (Basu, 2010). For OPB, the dirt in this biomass unavoidably influenced the yields, generating some uncertainty despite replication.

As previously outlined, the production and promotion of char is one of the objectives in this study for biochar production. The greatest char yield was produced by the OPB in all cases. The reasons could come from a set of features of this specific feedstock. It might be possible that its lignin content has influenced the char yield because lignin promotes char formation in comparison with cellulose or hemicellulose (Stefanidis et al., 2014). Nonetheless, it was not the only influencing factor. The particle size was the biggest in comparison with the rest of materials and it was aforementioned that it increment the char yield. Secondly, it was the biomass with higher ash content (see Table 1). This reason affects not only the weight but also the possibility of being catalysed by any of the inorganic components. Several authors have identified the influence of alkali metals like K and Na on pyrolysis and their presence promotes the char formation (Eom et al., 2012; Saddawi et al., 2012). The char from the OSB barely changes between the different working temperatures and has the lowest yield among the materials at 350 °C. The thermogravimetric studies showed a stronger and earlier devolatilisation of the OSB, explaining this behaviour and validating that the gas increase proceeded primarily from further cracking of the condensable vapours. The PWB and ASB presented the lowest char yields at 550 °C due to their high loss of volatile matter (Fig. 3) and low ash contents (Table 1).

Throughout the series of experiments, several factors were found to modify the yield and behaviour of the obtained products; some of these factors are linked to the heterogeneity of the feedstock and others with the pilot plant size when compared to laboratory scale experiments. Therefore, the standard deviation was calculated for yields (Table 3).

3.3.2. *Energy balance*

For the energy balanced assessment the main points of interest are the input energy or consumed energy during the pyrolysis process and the output energy or the energy of the products.

3.3.2.1. Input energy. The energy demand for the pyrolysis process is a key factor used to establish the energy balance for the process. This value depends on several factors, such as energy losses, working time, working temperature, type of feedstock and feeding rate. The main processing system features are shown in Table 2.

The energy losses in the reactor can be treated as constants, but they are proportional to the working time. Therefore, the energy losses are expected to be higher when the reactor works for longer periods to process the same amount of material due to their different feeding rates (kg/h); these differences are caused by their various bulk densities.

The effect of the temperature on ASB, OPB, PWB and OSB was assessed during the thermogravimetric studies and each biomass required more energy as the temperature increased. However, the findings were different in the pilot plant, due to its different working conditions; the thermobalance had a constant temperature ramp and was more accurate regarding temperature control, while the pilot plant feeding system utilised loads that entered the reactor after achieving the working temperature. Despite these differences, the data from TGA facilitated a better understanding of the pilot plant outcomes. The materials also showed different behaviours upon comparison. The ASB showed similar DSC

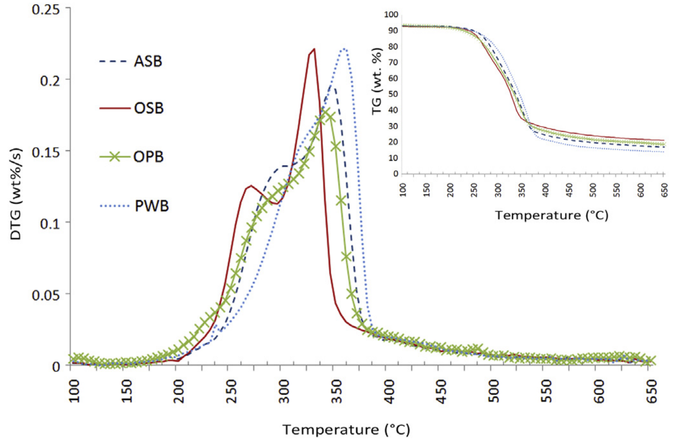

Fig. 3. TG and DTG curves for almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses.

Table 3
Yields (%), number of replicates (N) and standard deviations (σ) of the products of the pyrolysis process for almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses at the three studied temperatures.

Feedstock	N	T(°C)	Solid fraction		Líquid fraction		Gas fraction	
			(wt %)	σ	(wt %)	σ	(wt %)[a]	σ
ASB	2	350	29.09	0.41	22.79	0.82	48.12	0.41
	2	450	24.81	0.74	21.11	2.23	54.09	1.48
	2	550	21.81	0.13	17.27	0.18	60.93	0.30
OSB	2	350	27.89	2.76	21.76	5.17	50.35	2.41
	2	450	24.91	0.14	17.24	2.01	57.85	2.15
	2	550	24.37	1.24	8.81	4.49	66.82	3.25
OPB	2	350	41.05	10.45	26.74	6.50	32.21	3.95
	2	450	31.96	8.11	20.05	5.45	47.99	2.66
	3	550	29.30	5.80	23.24	3.45	47.47	9.24
PWB	3	350	30.73	2.90	32.17	5.15	37.10	2.97
	3	450	25.02	2.44	26.97	2.12	48.01	0.79
	3	550	19.08	1.19	13.62	1.00	67.30	1.90

[a] Calculated by difference.

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tendencies with similar ratios; its decomposition was likely more gradual than others and more independent of the system conditions. The OPB also exhibited increased consumption at increased temperature although it was not with similar DSC ratios. The OSB showed a higher consumption at 350 °C than at 450 and 550 °C due to the early and rapid devolatilisation (see Fig. 3) requiring more energy at low temperatures. Moreover, at 450 and 550 °C, which is where the thermogravimetric studies showed the aggregation of char (exothermic) as the dominant step, two strong phenomenona occurred at the same time in the reactor chamber, minimising the energy consumption. First, the loads at the entrance of the chamber required energy for their rapid decomposition. Second, the material, that had just devolatilised kept releasing energy due to the aggregation of char that occurred until the end of the residence time, causing instabilities that were revealed while monitoring the process. Finally, the PWB had higher consumption at 350 °C than 450 °C. The DSC studies showed an endothermic peak that was higher than the rest of materials from 360 to 380 °C (see Fig. 2). This peak might require more energy on the pilot scale at 350 °C because of the displacement of the peak at lower temperatures under different working conditions or the limitations in temperature control compared to the thermobalance system.

The feeding rate was influenced by the particle size. As previously mentioned, one of the purposes of this research was to reduce the energy consumed during pre-treatments. Therefore, the reactor was fed with the biomasses as received. Some differences were observed regarding the way they were presented and the consequences of the process. The OPB had the lowest feeding rate (see Table 2), increasing the processing time and the energy losses of the system proportionally. In addition, this material came with dirt from the pruning and collection stages, demanding additional energy input because this inert material was also heated. In comparison, the PWB was received as pellet and was therefore denser. This material required lower energy consumption because it was easy to treat, decreasing the energy losses linked to the extended working time required to treat the OPB. Moreover, ASB and OSB were treated as obtained: residues with a proper size for treatment while enhancing the feeding rate. These results suggest the grade of pre-treatment necessary must be assessed to perform the process and avoid the excessive energy consumption associated with the presentation of the raw material.

3.3.2.2. Output energy from pyrolysis products. The energy content of the biomasses was distributed through the pyrolysis process in three fractions to different degrees. Fig. 4 shows the percentage of the energy for each fraction as the working temperature increased. The main energy carrier was the char, decreasing in energy as the temperature rose. This finding can be attributed to the decreased yield instead of the lower heating value (LHV); the LHV increased as the temperature rose. The second energy carrier was the gas fraction and its energy content increased with the temperature; this carrier was notable for PWB at 550 °C. The main reason for this behaviour may be that the highest gas yield and gas components which had higher heating values. The last energy carrier was the liquid fraction that was characterised by the lowest yield, as well as its phase separation into heavy and light phases. The higher heating value (HHV) of the heavy phase ranged from 22.9 to 26.9 MJ/kg, depending on the type of biomass, with 12–21 % water. The light phase contained between 61 and 92 % water. The high water content is characteristic of liquids from biomass pyrolysis (Akhtar and Saidina Amin, 2012). This light phase ranges from 35 to 61 % of the total liquid fraction at low and high temperature, respectively, and depends on the raw material. The presence of the light phase increased with the temperature, promoting decarboxylation and dehydration reactions and increasing the water content of the reaction (Akhtar and Saidina Amin, 2012). The water content may

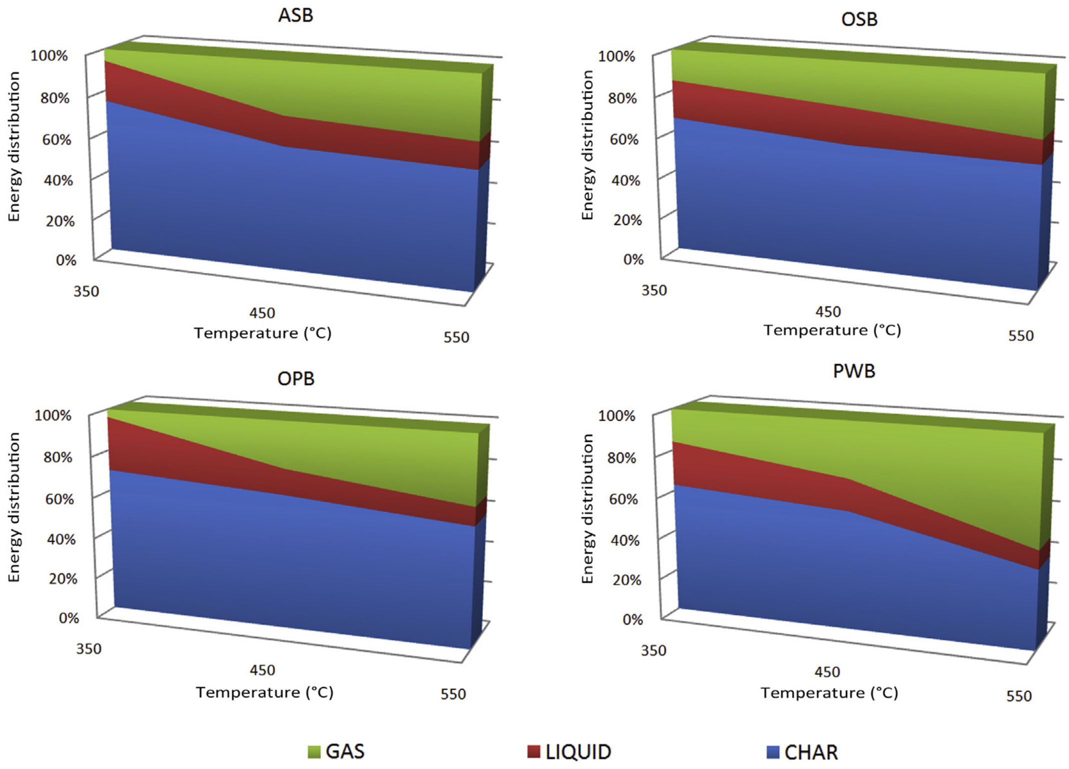

Fig. 4. Energy yield for the pyrolysis products from almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses at the three studied temperatures.

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limit the use of the total liquid fraction as a fuel because it affects the viscosity in a complex manner, diminishes the heating value and also modifies the density, stability, pH and homogeneity (Bridgwater et al., 1999).

3.3.2.3. Gas fraction composition for energy application. The gas fraction was previously mentioned as a considerable energy source due to its energy content. The main gases generated during devolatilisation were CO, CO_2, light hydrocarbons and H_2, as illustrated by Fig. 5; this figure shows the evolution of the gas components from different biomass sources when the temperature is increased. Both CO and CO_2 arose from the decarboxylation processes (Yang et al., 2007). The four materials increased CO production when the temperature was increased. The OSB and OPB exhibited their peak CO_2 at 450 °C, matching one of the CO_2 peaks linked to a hemicellulose decomposition profile identified by another author (Yang et al., 2007); this researcher investigated the thermal decomposition process of cellulose, hemicellulose and lignin in detail. The CH_4 and C_2–C_6 hydrocarbons increased as the temperature increased. These materials were formed from the cracking of hydrocarbons, particularly for the woody biomass. Moreover, the CH_4 was also apparent in all of the biomass decompositions because it proceeded from the decomposition of hemicellulose, cellulose and lignin at low, middle and high temperature ranges (Yang et al., 2007). Hydrogen was found only at medium and high temperatures. According to Neves et al. (2011), the hydrogen in the raw material was mostly converted into H_2 at temperatures above 500 °C, where the material is thermodynamically stable. The hydrogen was detected with the chromatograph in OPB, PWB and OSB, but not in ASB, at 550 °C. The N_2 came from the air remaining between the particles during the entrance of the material load; the N_2 content tended to decrease as the temperature increased. This behaviour is explained by the increased devolatilisation that promoted the increment of CO, CO_2, light hydrocarbons and H_2 content of the gas, decreasing the nitrogen percentage via dilution. OSB was the exception due to the deficient CO_2 formation at 550 °C relative to 450 °C, resulting in a less dilution.

The lower heating values (LHV) are shown in Table 4. The LHV increased when the temperature was increased due to the increase in devolatilisation and gas components that could provide better heating values (Sánchez et al., 2009). At low temperatures, the PWB exhibited the best LHV. At moderate and high temperatures, both woody biomass sources (PWB and OPB) produced the gas fraction with the highest LHV due to their higher hydrocarbons and hydrogen contents; these components conferred a high heating value, according to Fig. 5. Although the OSB showed the highest gas yield at low and medium temperatures, it did not present the highest LHV due to the low hydrocarbon (C_2–C_6 chains) and H_2 contents.

3.3.2.4. Assessment of a potential self-sufficient system. The properties of the gas and liquid fractions help while assessing a self-sufficient system. The gas fraction had variable gas components which might affect the conventional burning systems with specific gas requirements. Moreover, the liquid fraction had a high water content that may hinder its direct use. Nevertheless, if the vapours and steam presented in the gas flow were introduced in an adjacent combustion chamber before any condensation, all the available energy could be used. Table 5 shows the required energy for each test, the available energy in gas and liquid phases and the possibility of self-sufficient system. A self-sufficient system would be possible using only the gas fraction, except for ASB and OPB gases at 350 °C; both fractions would fulfil all the energy requirement of the process at all temperatures as well. Therefore, despite the increase in energy consumption that could utilise material with a low grade of pre-treatment from some waste biomasses during the pyrolysis

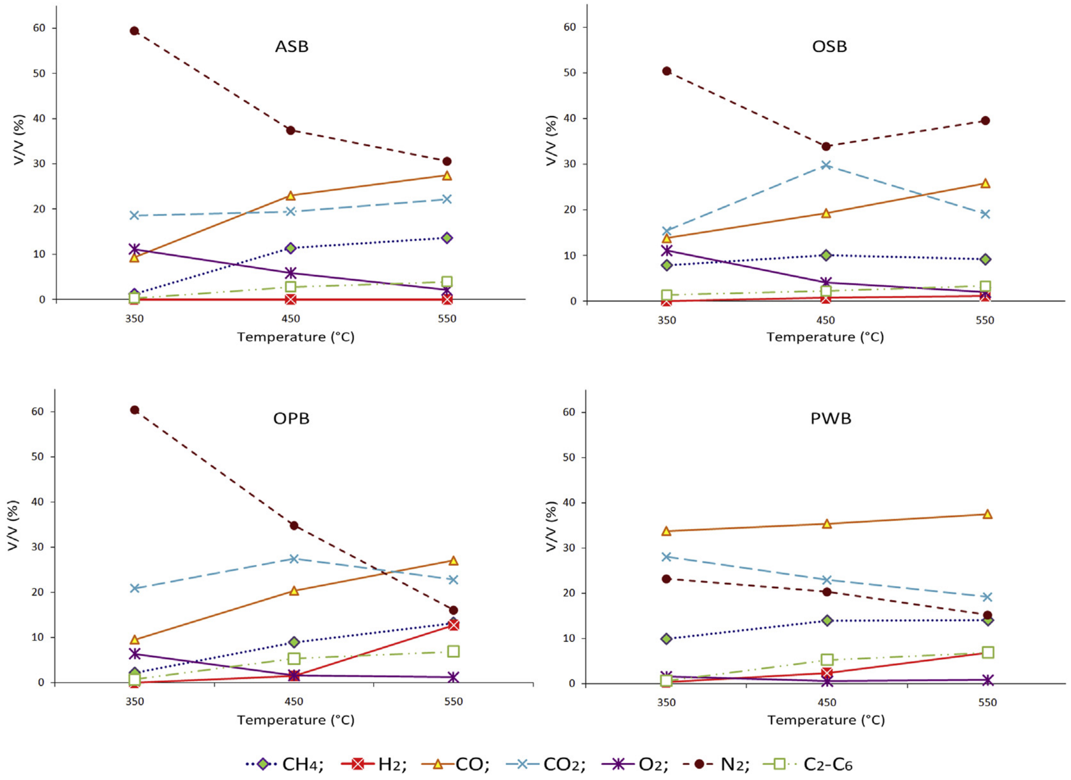

Fig. 5. Evolution of the gas composition (V/V %) from the pyrolysis of almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses versus the temperature.

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Table 4
LHV and density of gases from the pyrolysis of almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses at the three studied temperatures.

Feedstock T (°C)	ASB			OSB			OPB			PWB		
	350	450	550	350	450	550	350	450	550	350	450	550
LHV (MJ/m^3)	1.83	8.85	9.29	5.52	7.68	8.90	2.46	9.66	14.25	9.94	12.60	15.32
Density (kg/m^3)	1.46	1.51	1.54	1.44	1.55	1.52	1.47	1.54	1.40	1.65	1.57	1.24

Table 5
Preliminary assessment of a self-sufficient system from the gas and liquid fraction of the pyrolysis process for almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses at the three studied temperatures. The energy fulfilled criteria are pointed out for self-sustainable systems.

Feedstock	T (°C)	Required energy (MJ/kg)	Energy of gas (MJ/kg)	Energy of liquid (MJ/kg)	Energy of biochar (MJ/kg)	Self-sufficient system *only gas*	Self-sufficient system *gas and liquid*
ASB	350	0.81	0.60	2.09	8.06		•
	450	1.75	3.17	1.80	7.44	•	•
	550	2.66	3.67	1.55	6.92	•	•
OSB	350	1.79	1.93	2.37	8.54	•	•
	450	1.78	2.86	2.33	7.93	•	•
	550	1.30	3.92	1.50	7.82	•	•
OPB	350	1.59	0.54	3.78	10.19		•
	450	2.47	3.00	2.16	8.68	•	•
	550	2.97	4.82	1.29	8.42	•	•
PWB	350	1.80	2.31	3.12	9.25	•	•
	450	1.73	3.83	2.17	8.10	•	•
	550	1.94	7.95	1.34	5.76	•	•

process, a self-sufficient system would be able to sustain the process. In addition, surplus energy was identified; this energy could be recovered and used to increase the global process efficiency. For instance, the heat of the fumes that contribute to the surplus energy could be used to dry feedstock or produce heat for the surrounding facilities, using heat exchangers.

3.3.3. *Solid fraction properties*

Table 6 summarises the proximate and immediate analysis of the solid fraction from the four biomasses at the three temperatures for olive stone char (OSC), almond shell char (ASC), pine wood char (PWC) and olive-tree pruning char (OPC). When comparing the manner in which biomasses are degraded (Tables 1 and 6), pyrolysis provides a solid fraction that has lost its volatile matter and had become concentrated with the ashes and fixed carbon fractions. This behaviour is enhanced when the temperature is increased. The OPC had higher ash content than did the rest; no clear relationship was observed with the temperature in the ash content caused by the changes in dirt related to the collection of this biomass. The concentration in ashes should be a parameter to be controlled when char is intended for use as a fuel (McKendry, 2002). Nonetheless, it might have a neutral impact when added to soil.

The volatile matter in fuels is closely related to the facility for ignition while it can be used as a parameter to establish the degree of carbonisation for biochar. Biochar with copious volatile matter usually contains abundant phenolic compounds that are a source of C for microbial respiration (labile carbon) (Zimmerman and Gao, 2013; Major, 2010); biochar with low volatile matter contains pyranones, ethers and quinones as more stable carbon forms (Deenik et al., 2010; Major, 2010). The volatile matter varied from 32 to 17 % at 350 °C; 19 to 11 % at 450 °C; and 14 to 6 % at 550 °C. Consequently, the solid fraction obtained at 350 °C might not be useful for improving the soil properties while the solid fraction at 450 °C and 550 °C could be. However, further work is necessary to refine these conclusions as shown in part 2. If they cannot be used as biochar, the solid fractions have a low heating value ranging from 24.83 to 32.09 MJ/kg. Therefore, they also contain concentrated energy and could be used as fuel.

The molar H/C_{org} and O/C_{org} ratios can also give some information regarding the biochar stability. Fig. 6 represents the Van Krevelen diagram for the earlier evaluation of the char as a soil

Table 6
Characterisation of the almond shell char (ASC), olive stone char (OSC), olive-tree pruning char (OPC) and pine wood char (PWC) at the three studied temperatures.

Char T (°C)	ASC			OSC			OPC			PWC		
	350	450	550	350	450	550	350	450	550	350	450	550
Moisture	3.70	3.97	3.86	3.29	2.85	3.34	4.21	3.94	3.70	3.88	3.58	4.27
Volatile matter[a]	31.85	14.42	8.86	17.08	11.71	6.44	29.75	19.16	13.68	30.16	19.13	13.17
Ash[a]	2.21	2.19	3.12	1.55	1.64	1.91	8.22	8.90	7.71	1.36	1.70	2.48
Fixed carbon[a,c]	65.95	83.39	88.02	81.37	86.65	91.65	62.03	71.94	78.62	68.48	79.17	84.35
C[b]	76.41	86.60	90.39	84.30	87.93	90.83	73.85	82.90	86.29	79.46	85.16	88.41
H[b]	3.91	2.84	2.05	3.11	2.55	1.64	4.02	2.67	2.28	3.63	2.78	2.52
N[b]	0.29	0.38	0.42	0.31	0.35	0.37	1.14	1.21	1.04	0.34	0.37	0.43
S[b]	0.05	0.05	0.05	0.05	0.05	0.05	0.06	0.06	0.06	0.05	0.05	0.08
O[b,c]	19.34	10.12	7.09	12.22	9.12	7.11	20.93	13.16	10.33	16.51	11.64	8.56
LHV (MJ/kg)	27.69	30.01	31.74	30.62	31.85	32.09	24.83	27.16	28.75	30.34	30.64	31.16

[a] Percentage on a dry basis.
[b] Percentage on a dry, ash-free basis.
[c] Calculated by difference.

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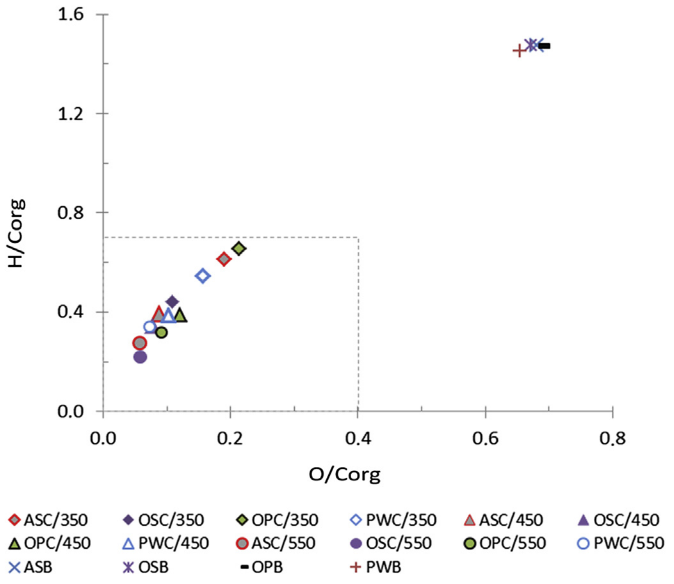

Fig. 6. Van Krevelen diagram from almond shell (ASB, ASC), olive stone (OSB, OSC), olive-tree pruning (OPB, OPC) and pine wood (PWB, PWC) biomasses and char from pyrolysis process at the three studied temperatures.

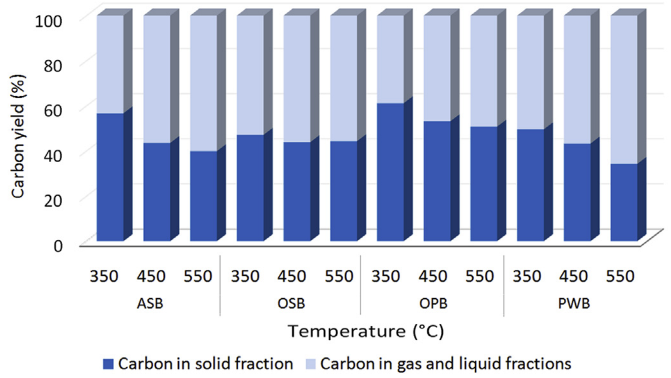

Fig. 7. Carbon recovery in the solid fraction from the pyrolysis of almond shell (ASB), olive stone (OSB), olive-tree pruning (OPB) and pine wood (PWB) biomasses at the three studied temperatures.

amendment. The H/C_{org} ratio is correlated with the degree of thermochemical alteration that produces fused aromatic ring structures in the material. The upper H/C_{org} limit of 0.7 is an intrinsic stability measurement for the material (IBI, 2014). Fig. 5 shows that the four biomass sources are quite far from the delimited area, meaning that they are easy to degrade in soil. The molar O/C_{org} ratio describes the stability in biochar. The oxygen content can drive chemical reactions and thus degradation potential (Spokas, 2010). The low molar O/C_{org} ratios generate a product with stable carbon. The ratios below 0.2 are typically the most stable, with an estimated half-life that exceeds 1000 years; ratios from 0.2 to 0.6 could have intermediate half-lives between 100 and 1000 years (Spokas, 2010). The studied chars were ≤ 0.2 O/C_{org}. Therefore, long half-lives are expected.

The effect of the pyrolysis on the carbon recovery versus the working temperature is shown in Fig. 7. The carbon content of the raw material is now distributed between the three pyrolysis fractions. The char contains from 76 to 91 % carbon (see Table 6); however, as the yield decreases, the amount of carbon recovered from the raw biomass also decreases (see Fig. 7) despite the increased carbon content in the chars obtained at higher temperatures.

After accounting for the previous information, the most appropriate biochar should meet diverse requirements, particularly high yield, low volatile content, high carbon content, high carbon recovery, and low H/C_{org} and O/C_{org} ratios, as well as high enough yields of gas and liquid to generate self-sustainable systems. As a result, part 2 is focused on the assessment of the quality of the produced chars as soil amendments, depending on the feedstock source and pyrolysis temperature. Recommendations for char production conditions and quality parameters are made based on the results obtained.

4. Conclusions

The slow pyrolysis process has been presented as residual biomass management looking for self-sustainable processes and low carbon technologies. The observed complexity of the process comes from the variations in chemical composition of the biomasses. Although their H/C and O/C ratios seem similar, their behaviour under pyrolysis is rather different even for the same biomass type (e.g. woody biomasses). The behaviour under TG tests has allowed explanation of the energy consumption phenomena and yield tendencies for each biomass in the large scale experiments. The "as received" conditions of the biomass is also a rolling factor in biomass processing as it has been shown with the effect of particle size or bulk density mainly affecting the processing time or the product yields. The pilot plant has shown that the main energy carrier is the char, but it is going to be studied as biochar. Nevertheless, a self-sustainable process has been identified utilizing the energy of liquid and gases, even with low grade pre-treatment and low working temperatures. The preliminary evaluation showed that all chars can be considered as potential biochars due to the fact that they have changed the structure into more stable forms (≤ 0.2 $O/C_{org.}$) and contain between 76 and 91 % of carbon of the raw biomass. Thus, it may behave as a carbon sink. Nevertheless, their properties as soil amendments should be carefully defined. The second part of this study addresses the agronomic quality of biochar (pH, surface area, aromaticity degree, etc.) to complete the evaluation of the sustainability of agriculture-bioenergy production systems.

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